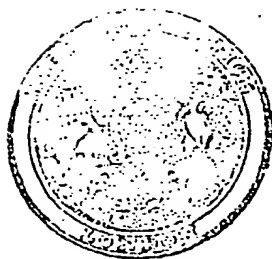


PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Coating Metals and Other Material with Stable Metal Oxides

We, NORTON GRINDING WHEEL COMPANY LIMITED, of Welwyn Garden City, Hertfordshire, a Company registered under the laws of Great Britain, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

- This invention relates to the coating of metals and other materials, such as graphite, with stable metal oxide as hereinafter defined or a mixture thereof. Many different metal oxides and combinations of such oxides can be used.
- One object of the invention is to provide a wear resistant surface on metal or other material. Another object of the invention is to provide a refractory surface on metal or other material. Another object is to provide metal or other material with a coating protecting it from oxidation.

- Another object of the invention is to produce components for gas turbines, jet engines, rocket nozzles and chambers and other components which are subjected to hot flame in use, by casting, forging, spinning, turning or machining the components to the desired shape (which may be complex) out of materials such as metal and graphite which can easily be wrought and thereafter coating the components with stable metal oxide or oxide combination which is resistant to the hot flame, resisting attrition by friction, oxidation and other chemical reaction and also being highly refractory, whereas the underlying metal or graphite does not have these properties.

- Another object is to provide a method of the type indicated which can be readily carried out with simple equipment and requiring no special skill. Another object is to provide a method for coating material with stable metal oxide or oxides which does not require the preheating of the material. Another object is to provide a thermal insulation coating on a piece of metal. Another object is to provide an electrical insulation coating on a piece of metal.

In the accompanying drawings illustrating

one type of fusing and spraying gun which can be used to coat materials with stable metal oxide by the process according to the invention,

Figure 1 is a side elevation of the gun, a portion of the casing being broken away to show the feeding mechanism,

Figure 2 is a sectional view taken along the line 2—2 of Figure 1,

Figure 3 is a simple electrical diagram illustrating how the rate of feed can be varied.

As conducive to a clearer understanding of the present invention it is noted that the mechanism for carrying out the coating process can have many different forms. For many years materials of various kinds have been coated with metal using metal spraying guns which apparently were originally developed in Switzerland. These guns were known as Schoop metal spraying guns and they were provided with means for feeding metal wire at a steady but variable rate, means for fusing the wire and means for atomizing the fused metal and projecting it as a spray.

Years ago attempts were made to spray metal oxides, in finely divided condition, that is to say as a powder, which was dropped into an oxyacetylene or oxyhydrogen flame thus to produce a spray of molten oxide. It was found, however, that in order to coat a metallic body with oxide the metal had to be heated before being coated.

We have discovered that a tenacious coating of stable metal oxide, for example alumina, zirconia or spinel can be formed on metal or graphite and on other substances by feeding a solid rod of such oxide into a high temperature blast of gas to fuse the oxide, to atomize it and spray it, the gas having sufficient velocity to atomize the molten oxide and to spray it on the metal or graphite or other substance, and that proceeding in this manner the metal or graphite or other substance does not have to be heated before the coating is applied. Furthermore the coating will not craze, crack, spall or peel.

We preferably provide rods of sintered alumina, zirconia or spinel, that is to say the

rods are of uniform composition made by sintering small particles together under high temperatures. Taking finely divided oxide material and providing a temporary binder, small diameter rods can be moulded under pressure in a manner now well known to the art, and thereafter the rods can be heated to a temperature to sinter the particles together while at the same time burning out the temporary binder. Strong refractory rods of pure oxide material are thus produced.

As an illustrative example of the process of the invention, we procured a metal spray gun constructed substantially in accordance with U.S. Patent No. 2,227,752 and which is readily available on the market. We removed the turbine mechanism and substituted a variable speed motor connected to the gun by a flexible drive. We also provided new feeding wheels more adaptable to feeding rigid rods than the original wheels intended for feeding flexible wire.

Referring now to Figure 1, the motor 10 had a base 11 secured to a table, not shown, and the gun had a grip 12 by means of which it could be held or clamped in place if desired. The motor 10 was connected to the input shaft 13 (see Figure 2) of the spray gun by means of a flexible drive shaft 14 enclosed in a flexible tube 15.

The shaft 13 had a worm, not shown, driving a worm wheel 20 on a shaft 21 having thereon a worm 22 driving a worm wheel 23 connected to a gear 24 meshing with a gear 25. We removed the feeding burrs (wheels) originally provided by the manufacturer of the gun and substituted rubber wheels 26 and 27 to feed the oxide rods 30 which were one-eighth inch in diameter. The gun was connected to an atomizing air hose 31 and an acetylene conveying hose 32 and an oxygen conveying hose 33. When the oxy-acetylene flame was lighted the rod 30 issuing through the nozzle 35 was fused. Referring to Figure 3, the rate at which the oxide rod was fed through the gun could be varied by rheostat 36 in the circuit for the motor 10. We had success using the alumina rods and spraying them at a feeding rate of 1.18 inches per minute and fusing and spraying the zirconia rods at a feeding rate at 1.456 inches per minute. In each case the rods were one-eighth inch in diameter.

It is unnecessary to describe the further mechanical details of the gun which we used as any other similar apparatus can be used.

Any kind of metal can be coated in accordance with this invention. We find it is desirable to sandblast most metals particularly cast iron and steel of any description prior to applying the coating. If this is done the coating can be applied with the greatest of ease and scarcely requires any skill at all. If the metal or graphite or other substance is not receiving any coating it is because the gun

is too far away from or too close to the object being coated. Obviously the gun should not be held so close to the object being coated that the flame will burn the object. In other words the object being coated should be held just off the end of the flame. With this proviso if coating does not appear the gun should be held a little closer. Usually the correct distance of the tip of the nozzle from the object to be coated is between one and two inches.

Coating of any thickness can be applied it being merely a matter of how much time is taken. As for gas pressure we find it is satisfactory to have the oxygen at 15 to 20 pounds, the acetylene at 15 to 20 pounds and the air at 60 pounds per square inch.

The above figures are for coating with alumina; in the case of zirconia the oxygen and acetylene are preferably at the same pressure but the air pressure is preferably at about 40 pounds per square inch.

For coating objects with spinel or other oxides, the air and acetylene pressures can be the same, the feed can be varied until a good coating is obtained, and for materials fusing below 2000° C. an air pressure of about 60 pounds would be preferred whereas for materials fusing above 2000° C. the pressure should be a little lower. As above stated the pressure for zirconia is found to be preferably at 40 pounds per square inch and as zirconia fused at 2700° C., a graph of the melting point of oxides on this slope will quickly give the answer as to what pressure should be used.

We have mentioned coating material with alumina, zirconia and spinel. Alumina coatings and zirconia coatings are especially desirable for many practical purposes.

Spinel of the general formula $R^I O \cdot R^{II} O_3$ in which R^I can be any of magnesium, iron, zinc, manganese and nickel and R^{II} can be any of aluminium, iron and chromium are well known. The commonest and best known type is magnesium-aluminium spinel, commonly called "spinel". Any of these or complexes thereof can be used provided they do not contain uncombined iron oxides in substantial amount. For example many pairs of spinels form solid solutions with each other in all proportions. The aluminium spinels form a series all of the members whereof are miscible with each other. The iron spinels in which the iron oxide is Fe_2O_3 form another series all of the members of which are miscible with each other, and so do the chromium spinels. Furthermore rods made of sintered mixtures of the spinel oxides in the right proportions can be used in the invention and the coating will be a true spinel. The spinel oxides are soluble in the spinels so that the spinel can contain excess of a spinel oxide. This is especially true of alumina which can be readily dissolved in the aluminium spinels. But we can coat with any stable metal oxide and in

this connection we use the widely accepted definition of a metal which is that it is a good conductor of electricity and forms a basic or amphoteric oxide. This definition excludes silicon, germanium, boron, carbon, phosphorus, arsenic and sulphur. Suitable oxides (leaving out very expensive and rare metal oxides although they too can be used) are alumina, barium oxide, beryllium oxide, lime, cobalt oxide, niobium oxide, magnesia, manganese oxide, molybdenum oxide, nickel oxide, strontium oxide, tantalum oxide, thorium oxide, titanium, uranium oxide, vanadium oxide, zinc oxide and zirconia. Many of these metals have more than one oxide and all can be used which are stable. It is to be understood that oxides referred to herein as stable are those which will not be reduced to metal

by fusion in the flame or volatilize to any appreciable extent at fusion temperature. Since iron oxides themselves are reduced to metal by the fusion, when they are not in combination with other oxide, they are omitted from the above list.

Silica is not in the list as silicon is not a metal and also silica is glass forming, and when fused and blasted forms fibers. But minor percentages of silica can be tolerated, for example emery can be used. Mixtures and solid solutions as well as double, ternary and quaternary oxides can be sprayed in accordance with the invention. For example discrete particles of alumina and zirconia can be sintered together to make a rod which can be used. Any of the following minerals in rod form can be used to make the coating:—

Chromite	-	-	-	-	-	FeO.Cr ₂ O ₃
Chrysoberyl	-	-	-	-	-	BeO.Al ₂ O ₃
Emery	-	-	-	-	-	mix. of corundum, magnetite, hematite, quartz and spinel
Gahnite	-	-	-	-	-	ZnAl ₂ O ₄
Geikielite	-	-	-	-	-	(Mg,Fe)O.TiO ₂
Hercynite	-	-	-	-	-	FeAl ₂ O ₄
Ilmenite	-	-	-	-	-	FeO.TiO ₂
Lewisite	-	-	-	-	-	5CaO.2TiO ₂ .3Sb ₂ O ₃
Picotite	-	-	-	-	-	(Mg,Fe)O.(Al,Cr) ₂ O ₃
Plenonaste	-	-	-	-	-	(Mg,Fe)O.Al ₂ O ₃
Pseudobrookite	-	-	-	-	-	2Fe ₂ O ₃ .3TiO ₂
Pyrochlore	-	-	-	-	-	Nb ₂ O ₅ .(Ti,Th)O ₃
Spinel	-	-	-	-	-	MgO.Al ₂ O ₃
Tantalite	-	-	-	-	-	(Fe,Mn) [(Nb,Ta)O ₃] ₂
Tapiolite	-	-	-	-	-	Fe(Ta,Nb) ₂ O ₆
Thorianite	-	-	-	-	-	(Th,U)O ₂ (+He,Ce,La,Pb,Fe)
Uraninite	-	-	-	-	-	UO ₃ .UO ₂ .PbO

Those minerals containing water of crystallization will lose this water on being sintered into rod form but they are nevertheless usable in the invention. Mixtures of the foregoing minerals or mixtures of the stable metal oxides previously referred to may be employed and mixtures of the minerals must consist substantially of stable metal oxides. As will be seen from the examples, minor proportions of other elements such as silicon, halogen or helium are not excluded from the starting material but some thereof may be eliminated during the sintering into rod form.

If the expense is justified, steel can be protected from the weather by a permanent coating of oxide applied in accordance with this invention. Whereas a coating of paint lasts only for a limited time, a coating of oxide applied according to the invention will resist attack by wind, rain and sun almost indefinitely.

By the word "rod" we intend to include rods square or triangular in cross section and hexagonal rods as well as round ones. Also other shapes can be used.

In the specific disclosure the molten oxide is atomized by a blast of air. This can be referred to generically as a gas since other gases would serve equally well. In some cases the

combustible gas and the combustion supporting gas can have enough pressure to atomize the molten oxide. This in a sense is true in the illustrative example because the air blast assists in supporting combustion, that is to say it provides oxygen additional to that entering through the hose.

Our method or process can also be used to coat ceramic materials. Thus crucibles can be made more refractory and less pervious by coating them with a pure refractory oxide such as alumina or zirconia. Bricks can be made more resistant to corrosion by hot gases by coating them with alumina or zirconia. Batts and kiln furniture can be given longer life by coating them in accordance with the invention.

Sintered oxide material can itself be coated with the same or a different oxide according to the invention. In some cases this is advantageous. A crucible, beaker or other container can be made of alumina by moulding the white pure crystalline alumina, or by moulding the white pure amorphous (Bayer process) alumina or by moulding mixtures of these varieties (each over 99% pure). About 1% of Bentonite (and water) is frequently added to make the mix plastic enough for easy moulding. Then the moulded article after drying, is fired. For

some uses the article will be too porous. By coating the article with alumina in accordance with the invention this defect is overcome. Such an article comes under the generic description "ceramic material." All ceramic materials can be coated in accordance with the invention. Bricks, batts and kiln furniture also come under the generic description "ceramic material."

10 For guided missiles, rockets and the like, parts can be made out of graphite which is refractory and then coated with stable metal oxide such as aluminium oxide according to the invention thus to protect the graphite from oxidation. The advantage of using graphite is that it is easily machined.

15 It is well known that the turbine blades of jet engines are very expensive to make and have to be replaced at very frequent intervals. By forging refractory metal such as molybdenum a heat resistant blade which is not brittle can readily be produced while forging and polishing will produce an accurate enough blade for practical purposes. However these blades will gradually deteriorate in the hot flame by oxidation. We can coat such blades with oxide according to this invention thus producing a superior blade. Because of its refractory properties, we prefer to coat such blades with zirconia and we prefer the stabilized zirconia containing from 3% to

6% of lime which produces substantially cubic crystal structure. Such stabilized zirconia may be made in accordance with the Specification of U.S. Patent No. 2,535,526.

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What we claim is:—

1. Process for coating a material with a stable metal oxide as hereinbefore defined or a mixture of such oxides alone or combined with other materials to form a heat stable substantially wholly metal oxide mixture comprising feeding a rod of said oxide into a flame hot enough to melt the oxide, atomizing the molten oxide with a blast of gas as it is melted, and spraying the atomized molten oxide onto the material to be coated.

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2. The process as claimed in claim 1 in which the rod employed is of sintered particles of metal oxide.

3. Process as claimed in claim 1 wherein the material receiving the coating is a metal.

4. Process as claimed in claim 1 wherein the material receiving the coating is graphite.

5. Process as claimed in claim 1 wherein the material receiving the coating is a ceramic material.

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6. Articles coated with a stable metal oxide as hereinbefore defined or a mixture of such oxides, when prepared by the process hereinbefore described and claimed.

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MARKS & CLERK.

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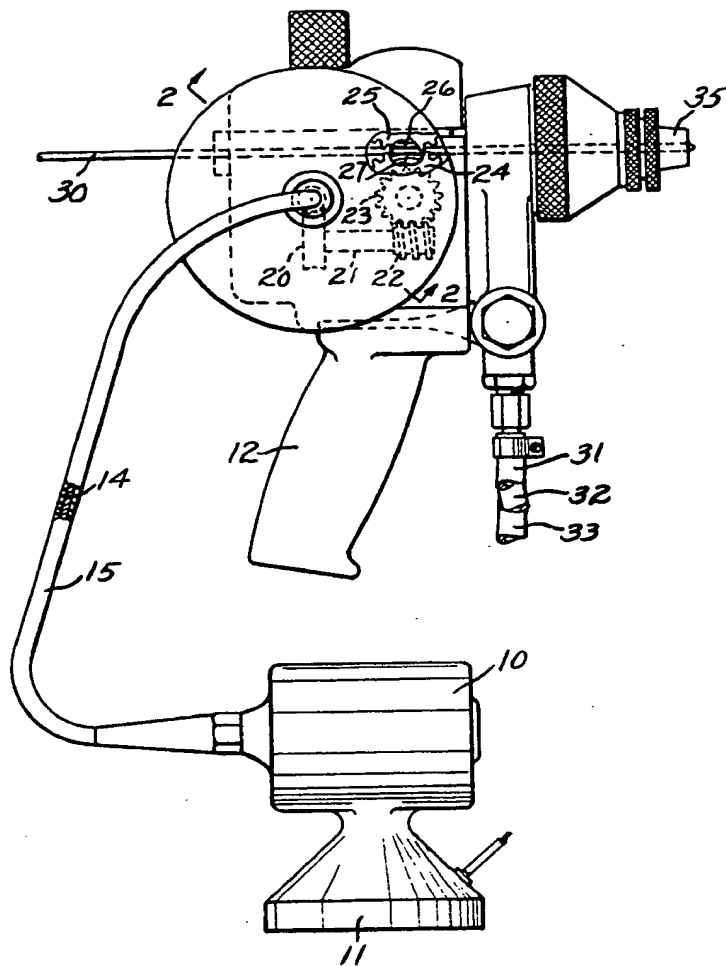


Fig. 1

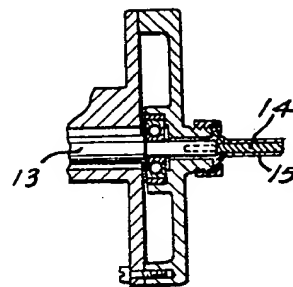


Fig. 2

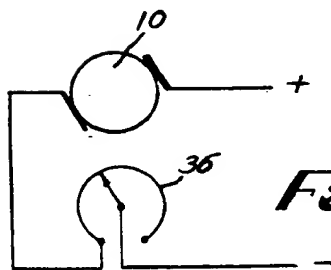


Fig. 3

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